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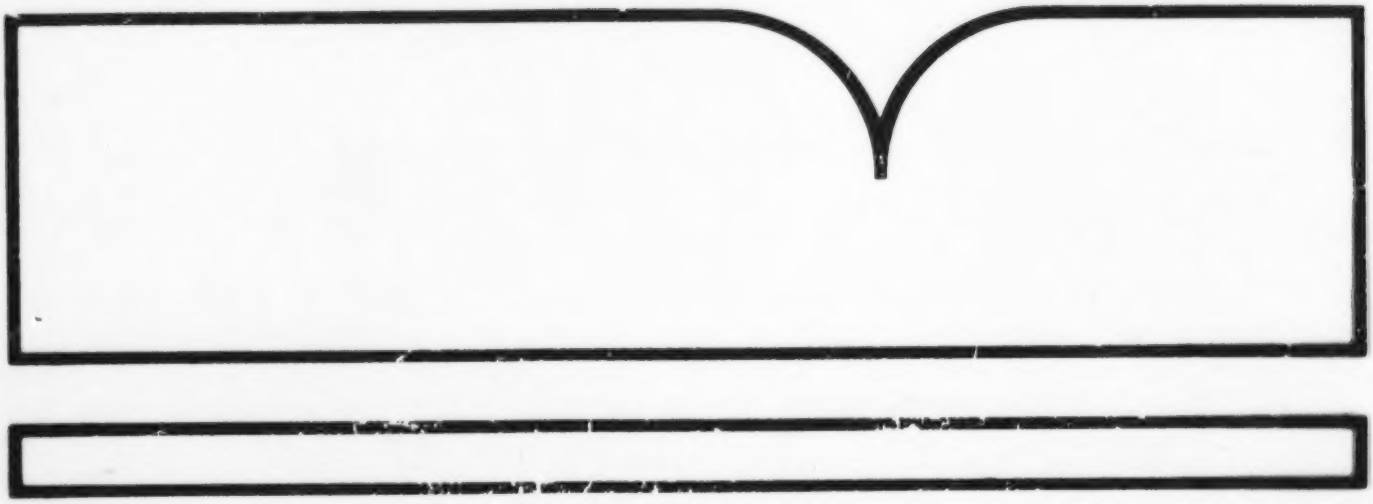

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16. ABSTRACT

A study was conducted to identify the specific organic reaction products of natural aquatic humic materials with selected oxidants ($KMnO_4$, HOCl, ClO_2, O_3 and monochloramine). Reaction products were identified by GC/MS after solvent extraction and derivatization. The two most reactive oxidants in terms of the number of identified products and overall yields were $KMnO_4$ and HOCl.

The macromolecular structure of aquatic humic and fulvic acids inferred from $KMnO_4$ studies may consist of (a) single-ring aromatics with mainly three to six alkyl substituents, carboxylic acid, ketone, or hydroxyl groups, (b) short aliphatic carbon chains, and (c) polycyclic ring structures.

The principal chlorination products identified were, in order of decreasing abundance, trichloroacetic acid, chloroform, and dichloracetic and dichlorosuccinic acids. For fulvic acid, the total yield of identifiable products was approximately 14 wt% of organic reactant (compared with 25 wt% for $KMnO_4$). Chlorine dioxide produced fewer identifiable reaction products than chlorine, with product composition dominated by C_4-C_{10} dibasic aliphatic acids. Chlorinated products of ClO_2 included trace amounts of dichloroacetic acid, chloromalonic acid, and chlorosuccinic acid. No products of the reaction of monochloramine with fulvic acid were identified by GC/MS.

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ENVIRONMENTAL RESEARCH BRIEF

Chemical Reactions of Aquatic Humic Materials with Selected Oxidants

R. F. Christman[1], J. D. Johnson, D. S. Millington, and A. A. Stevens[2]

Abstract

A study was conducted to identify the specific organic reaction products of natural aquatic humic materials with selected oxidants ($KMnO_4$, HOCl, ClO_2, O_3, and monochloramine). Fulvic and humic acid fractions were isolated from two southeastern U.S. surface waters using a combination of XAD-8 adsorption, acid precipitation, salt removal, and freeze drying. One or both fractions were exposed to each oxidant under controlled laboratory conditions at various oxidant/carbon molar ratios ($KMnO_4$, 0.75 to 2.2; HOCl, 4; ClO_2, 1.0; O_3, 4.8 to 7.3; monochloramine, 2.0 and 10.0). The principle objective was qualitative identification of reaction products; therefore strict efforts were not made to use reactant concentrations at water treatment plant levels or to keep oxidant/carbon ratios at identical levels for the different oxidants studied. Reaction products were identified by gas chromatography/mass spectrometry (GC/MS) after solvent extraction and derivatization. The two most reactive oxidants in terms of the number of identified products and overall yields were $KMnO_4$ and HOCl, though products were identified after exposure to ClO_2 and O_3. Certain similarities exist among the oxidation products identified from all oxidants, though the presence of chorine in reaction products depends on its presence in the oxidant.

The macromolecular structure of aquatic humic and fulvic acids (inferred from the nature of NaOH and $KMnO_4$ degradation products) may consist of (a) single-ring aromatics with mainly three to six alkyl substituents, carboxylic acid, ketone, or hydroxyl groups, (b) short aliphatic carbon chains, and (c) polycyclic ring structures, including polynuclear aromatics, polycyclic aromatic-aliphatics, and fused rings involving furan and possibly pyridine. Though the structural relationships between these fragments could not be established, these fragments are believed to be associated with humic macromolecules through carbon-carbon linkages.

The degradation products of fulvic and humic fractions from two water sources were qualitatively similar to each other, but some quantitative differences were found. The differences found between fulvic and humic fractions isolated from each source were smaller than the differences between the fractions isolated from the different sources.

The principal identified chlorination products of the fulvic and humic acid samples studied were, in order of decreasing abundance, trichloroacetic acid, chloroform, and dichloroacetic and dichlorosuccinic acids. For fulvic acid, the total yield of identifiable products was approximately 14 wt% of organic reactant (compared with 25 wt% for $KMnO_4$). The principal products accounted for approximately 4 wt% of original total organic carbon (TOC). Of these, product composition was approximately 69% trichloroacetic acid, 19% chloroform, 9.5% dichloroacetic acid, and 4.5% dichlorosuccinic acid, based on product carbon per gram of starting fulvic acid. Thus trichloroacetic acid (not chloroform) was shown to be the dominant chlorination product. Collectively, these four products accounted for 53% of the system total organic halogen (TOX).

Chlorine dioxide produced fewer identifiable reaction products than chlorine, with product composition dominated by C_4-C_{10} dibasic aliphatic acids. Chlorinated products of ClO_2 included trace amounts of dichloroacetic acid,

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monochloromalonic acid, and monochlorosuccinic acid. No products of the reaction of monochloramine with fulvic acid were identified by GC/MS.

This Research Brief was developed by the principal investigators and EPA's Municipal Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in the reports and publications listed at the end.

Introduction

Humic substances account for significant but variable proportions of the organic matter in soils and sediments and of the soluble organic matter in fresh and sea waters. Despite extensive research concerning the formation and environmental impact of waterborne organics, the chemical structures of aquatic humic substances are still not known to the desired level of certainty.

These natural products are apparently acidic, hydrophilic, complex materials that range in molecular weight from a few hundred to many thousands. Humic materials isolated from soils have been extensively studied, but it cannot be presumed that aquatic humic materials are similar except for chemical complexity. Degradation studies of soil humic acid have produced evidence of both aromatic and aliphatic constituents, but few degradation studies have been conducted on aquatic humics. Furthermore, it is not known whether aquatic humic and fulvic materials isolated from different sources exhibit chemical similarities.

Our experimental approach was therefore to expose natural humic and fulvic acid preparations to a nonhalogenated oxidant (alkaline $KMnO_4$) under controlled conditions. Knowledge of the yield and reaction product distribution should be useful for (a) increasing our understanding of the macromolecular structures of undergraded humic and fulvic materials, (b) determining the differences that may exist between humic substances from waters of different geographical locations, and (c) establishing a baseline of oxidation products with which chlorination products can be compared.

Certain experimental procedures are common to all aspects of this research. The XAD-8 isolation/purification process and the GC/MS systems employed are fully described in project publications (6,8,11). Except where specifically stated in these publications, GC/MS identifications were based on a set of criteria that includes the following for each compound: (a) electron impact (EI) mass spectrum, (b) chemical ionization (CI) mass spectrum for molecular ion confirmation, (c) elemental composition of major ions in the EI spectrum by means of low resolution, accurate mass measurement, (d) comparison of mass spectra with authentic speciments when available, and (e) comparison of GC retention time with that of an authentic specimen when available. Several factors in the analytical protocol of this research were important because many of the compounds identified are not available in mass spectral libraries. These factors are the use of capillary GC columns, rapid MS scan rates (generally 1 to 2 sec, compatible with the capillary GC profiles), use of double-focusing mass spectrometer, and the acquisition of accurate mass data without serious compromise to sensitivity or scan speed by using low resolution.

$KMnO_4$ Oxidation and Base Hydrolysis

The structures and yields of more than 70 compounds were determined in the product mixtures of fulvic and humic acid fractions exposed to NaOH hydrolysis and/or $KMnO_4$ oxidation (1,8). These products were classified, according to structural similarity, into the six groups shown in Table 1. The product distributions and overall yields for fulvic and humic acid samples from the two different sources were remarkably similar. The maximum yield of GC/MS detectable degradation products was approximately 25 wt% of starting material. Loss of volatiles (presumably CO_2) during oxidation was estimated at 20% to 25% of the original TOC, so that overall accountability of degradation products can be estimated as 35% of original TOC if it is assumed that identified products average 50% carbon. Thus only about one-third of starting material is represented by the identified compounds, though most of the chromatographable material was identified (see Table 1).

Except for Black Lake fulvic acid, aliphatic dibasic acids were the major base hydrolysis products for all the humic acid and fulvic acid samples. All of the base hydrolysis products identified were also present in permanganate oxidation products, but carboxyphenylglyoxylic acids were not found in the base hydrolyzed samples.

Permanganate oxidation of both fulvic and humic acids produced benzenecarboxylic acids as the dominant identified product category with the tri-, tetra-, and pentacarboxy acids presenting the principal substitution patterns. Fulvic and humic acids also gave high relative yields of oxalic, malonic, and succinic acids.

A significant difference was found among the aliphatic acid products. Most of the monobasic acids and the long-chain dibasic acids that were identified among the humic acid oxidation products were not detected in those of fulvic acid samples. This difference may indicate that the long-chain acids were associated with the less soluble hydrophobic humic acid macromolecules and were released as the humic acid macromolecules were degraded.

Under the conditions of experiments conducted in this study, the permanganate oxidation is believed to oxidize the alkyl side chains of arenes (aliphatic-aromatic compounds) and result in the formation of aromatic acids and saturated aliphatic acids. the permanganate oxidation data indicate that the principal number of alkyl constituents on the aromatic rings in the humic macromolecule is in the range of three to six to account for the predominance of the benzenepolycarboxylic acid derivatives. Two facts support the hypothesis that the length of these interaromatic alkyl chains may be relatively short. First, the C_2-C_4 aliphatic dibasic acids dominate the dibasic acid structures found. Second, the increase of benzenecarboxylic acid yield for $KMnO_4$ (compared with NaOH hydrolysis) is significantly greater than the increase in aliphatic dibasic acid yield. This result could occur if some of the alkyl bridges were short enough to yield only aromatic acids and CO_2 after oxidation. The survival of some long-chain dibasic acids after $KMnO_4$

Table 1. Summary of Results of $KMnO_4$ Oxidation and NaOH Hydrolysis of Aquatic Humic Acids and Fulvic Acids from Black Lake and Lake Drummond*

Compound Class	Black Lake				Lake Drummond			
	$KMnO_4$ Oxidation		NaOH Hydrolysis		$KMnO_4$ Oxidation		NaOH Hydrolysis	
	HA†	FA	HA	FA	HA	FA	HA	FA
Benzenecarboxylic acid methyl esters (29 compounds)	142.71	127.77	5.36	5.56	110.71	104.14	2.96	4.03
Furancarboxylic acid methyl esters (5 compounds)	13.61	9.98	0.14	0.16	21.10	26.64	0.36	0.38
Carboxyphenylglyoxylic acid methyl esters (8 compounds)	4.49	4.70	0.00	0.00	5.77	5.61	0.00	0.00
Aliphatic monobasic acid methyl esters (14 compounds)	4.07	0.82	0.72	2.49	14.84	6.14	0.54	1.99
Aliphatic dibasic acid methyl esters (14 compounds)	47.57	56.48	10.62	4.57	98.06	98.07	11.30	5.66
Aliphatic tribasic acid methyl esters (5 compounds)	0.62	1.47	0.29	0.39	4.94	4.52	0.45	0.51
Sum	213.07	201.22	17.13	13.17	255.42	245.12	15.61	12.57
Identified Percentage of Total GC Peak Area	88	91	71	73	86	88	63	69

*Yields (mg) resulted from 1.0 g of starting humic samples.
†FA, fulvic acid; HA, humic acid.

is established by the complete data, but it is not possible to evaluate the possibility that successive terminal oxidation of longer alkyl substituents could produce the same result.

An attractive assumption is that most of the carboxyl groups observed among these products constitute sites of carbon-to-carbon linkages in the undegraded macromolecule. This assumption is supported by the data in Table 1, which show that the total yield of acids produced by base hydrolysis is much lower. Some of the acid groups must be bound originally in ester linkages, probably with other aromatic moieties (to account for base hydrolysis yields). But most of the alkyl constituents of aromatic rings must be carbon chains, which resist sodium hydroxide hydrolysis. In addition, some of the carboxylic acids must be present as free groups in the undegraded macromolecule to account for the acidity of aquatic humics.

In general, the predominant products found in Black Lake samples are also the predominant products in Lake Drummond samples. Based on the results of this study, aquatic humic materials from the two sources are believed to be qualitatively similar, but quantitative variations were observed in the composition of humic degradation mixtures from the different sources. Whether these variations are related to seasonal changes, various stages of the humification process, or vegetative conditions indigenous to the source is not known.

Reaction with Chlorine

More than 100 reaction products were identified from exposure of humic acid to chlorine at a pH of 12 and from exposure of fulvic acid to chlorine at neutral pH (4,7,10,13). Principal aliphatic products (only the C_4 chain length and less) are shown in Table 2. Concentrated ether extracts of the fulvic acid reaction products were light green, had a sweet/acid odor reminiscent of chloroform or some chorinated acid, and reacted vigorously with diazomethane. Blank extracts were colorless, had no such odor, and had little visible reaction with diazomethane. In these respects, the concentrated fulvic acid samples and blanks resembled their counterparts from the high-pH humic acid work.

The initial HOCl/C molar ratio for the neutral pH fulvic acid reaction was 4, like that of pH 12 humic acid work. This pH 7 reaction with chlorine was apparently more rapid than the pH 7 humic acid high-pH reaction, judging from the rates of color bleaching. The pH 7 fulvic acid chlorine exposures were therefore held 24 hr, while humic acid high-pH exposures were allowed to reach 48 hr.

The majority of the pH 7 fulvic acid chlorine reaction products contained chlorine, whereas most of the pH 12 humic acid chlorine reaction products did not. In addition, many of the non-chlorine-containing fulvic acid products were present in the system control or sample blank. An adequate system control for the humic acid experiments was impossible to obtain, but the reaction products contained relatively large amounts of fatty acids (C_{16} dominant) that were not observed in the fulvic acid system controls.

Nearly all of the products identified in the humic acid experiment were methyl esters, presumably derived from the methylation of mono- and polybasic acids. These included mono- and dibasic, saturated and unsaturated, chlorine-substituted and unsubstituted acids. Most of the more than 100 compounds identified were not chlorinated; however, di- and trichloroacetic acid, dichlorosuccinic acid, and dichloromaleic and dichlorofumaric acid were formed in especially high yield. A large number of mono- and dibasic unchlorinated aliphatic acids from acetic and oxalic acid up to the C_{27} monobasic fatty acid were identified. The dibasic unchlorinated aliphatic acids were generally of low molecular weight (C_2-C_{10}). These aliphatic acids may be

ring-cleavage products and were present in relatively low yield. Benzenecarboxylic acids (including mono- to hexacarboxy acids in all isomers as well as small quantities of methyl-substituted aromatic acids and isomers of carboxyphenyl-glyoxylic acid) were also detected. Noticeably missing from the aromatic series were chlorine-substituted aromatic acids and aromatic acids with aliphatic side chains other than methyl. This pattern is similar to that found with permanganate oxidation, suggesting that chlorine in alkaline solution is capable of oxidizing side chains down to terminal carboxyl groups on the aromatic ring.

Several general features of the fulvic acid chlorination product distribution can be stated. First, except for chloroform and chloral, all components were methyl esters. A reasonable assumption is that they were free acids in the original aqueous sample, which serves to explain the diazomethane reaction. Second, unlike the pH 12 humic acid chlorination products, most of the pH 7 fulvic acid degradation products contained chlorine. They include chloroform; chloral; methyl mono-, di-, and trichloroacetate; dimethyl dichloromalonate; dimethyl dichlorosuccinate; dimethyl dichloromaleate; methyl 2,2-dichloropropionate; dimethyl chlorosuccinate; dimethyl chloromaleate; and various other less abundant compounds. Even some bromodichloromethane was formed, which must result from bromide ion impurity activated by HOCl. No chlorinated aromatic products were found.

Finally, most of the compounds from the fulvic acid reactions not containing chlorine were aromatic. They included various isomers of dimethylphthalate; benzene tricarboxylic acid trimethyl ester; benzene tetracarboxylic acid tetramethylester; and other aromatic methyl esters. These compounds did not clearly result from the chlorination reaction, since the sample blank or system control revealed their presence in similar quantities. Derivatives of phenylglyoxylic acid were found in the chlorinated reaction mixture (not in system control), an interesting group of structures. Confirmation could not be achieved in these samples, since no standards were available. They were found in the humic acid chlorination product extract as well as in potassium permanganate degradation product mixtures from aquatic humic and fulvic acids (10). Liao et al. proposed that such compounds can result from the oxidation of fused ring systems present in the humic (or fulvic) macromolecule (8).

A direct comparison of the yields of various compounds from the fulvic and humic acid chlorinations is unrealistic, since different reaction times were used. But both reactions clearly produce extremely similar products that contain a predominance of small chlorinated acids. TOX analyses on the concentrated ether extracts revealed that the fulvic sample contained 60% more organically bound chlorine than the humic sample, even though the reaction time of the latter was twice as long. This observation agrees with the expected greater electrophilic substitution of HOCl present at the more acidic pH values compared to the OCl^- present at pH 12.

The yields of the four principal chlorination products of fulvic acid were estimated initially by adding known quantities of an internal standard (methyl-*p*-chlorobenzoate) to ether extracts and measuring GC/MS peak-area ratios derived from selected ion current chromatograms (e.g., 117/139 for trichloroacetic acid). Actual weights of compounds of interest were then calculated from standard curves, and accurate concentrations in the aqueous reaction mixture of the two principal products (trichloroacetic acid and chloroform) were then determined by validated methods. An isotope dilution method developed in our laboratory (13) was used for trichloroacetic acid, and the standard EPA purge and trap method was employed for chloroform.* Yield values are summarized in Table 3. The values for the two minor products in Table 3 are probably underestimated since they were determined only in the ether extract.

The data establish that trichloroacetic acid (and not chloroform) is the dominant reaction product, and that the

Table 2. Short-Chain Chlorination Products of Aquatic Humic and Fulvic Acids

Formula	Name (Common)	Confidence*
$CHCl_3$	trichoromethane (chloroform)	b
$CHBrCl_2$	bromodichloromethane	b
CCl_3CHO	trichloroethanal (chloral)	b
H_2CClCO_2H	chloroethanoic acid (chloroacetic acid)	b
$HCCl_2CO_2H$	dichloroethanoic acid (dichloroacetic acid)	b
CCl_3CO_2H	trichloroethanoic acid (trichloroacetic acid)	a
$CH_3CCl_2CO_2H$	2,2-dichloropropanoic acid	b
$CCl_2{=}CHCO_2H$	3,3-dichloropropenoic acid	c
$CCl_2{=}CClCO_2H$	trichloropropenoic acid	d†
$HO_2CCCl_2CO_2H$	dichloropropanedioic acid (dichloromalonic acid)	a
$HO_2C(CH_2)_2CO_2H$	butanedioic acid (succinic acid)	c
$HO_2CCH_2CHClCO_2H$	chlorobutanedioic acid (chlorosuccinic acid)	c
$HO_2CCCl_2CH_2CO_2H$	2,2-dichlorobutanedioic acid (2,2-dichlorosuccinic acid)	c
$HO_2CCH{=}CClCO_2H$	cis-chlorobutenedioic acid (chloromaleic acid)	a
$HO_2CCCl{=}CClCO_2H$	cis-dichlorobutenedioic acid (dichloromaleic acid)	a
$HO_2CCCl{=}CClCO_2H$	trans-dichlorobutenedioic acid (dichlorofumaric acid)	a

*a. Confirmed: EI spectrum and GC retention time comparison with authentic specimen.
b. Confirmed; EI spectrum comparison with authentic specimen.
c. Confident; EI spectrum, CI spectrum, no authentic specimen available.
d. Tentative; data relatively incomplete in some respect.
† Observed only in fulvic acid samples.

*Method 501.1, USEPA, Cincinnati, Ohio 45268

Table 3. Yields of Fulvic Acid Chlorination Products

Product	mg Product/g Fulvic Acid	mg Product C/g Fulvic Acid C	Percent Original TOC	Percent Final TOX
Trichloroacetic acid	90.3	13.3	3.0	32.1
Chloroform	38.2	3.8	0.8	17.3
Dichloroacetic acid	10.2	1.9	0.4	3.6*
Dichlorosuccinic acid	3.4	0.9	0.2	---
Total	142.1	19.9	4.4	53.0

**Sum of dichloroacetic and dichlorosuccinic acids.*

four chlorinated products shown in Table 3 collectively account for 53% of the observed TOX (13).

Reaction with Other Oxidants

None of the other oxidants investigated in this study produced appreciable amounts of degradation products with aquatic fulvic acid compared with the permanganate and chlorine product data. Small amounts of products were identified with chlorine dioxide and ozone.

Reactions between ClO_2 and fulvic acid at pH values of 3 and 7.8 were found to be rapid but limited. Neither increased oxidant concentrations nor reaction times of up to 24 hr seemed to influence the extent of reaction. Recovery of TOC after reaction termination average 70% under both pH conditions; thus, an average of 30% of the original fulvic carbon was apparently converted to CO_2 or other extremely volatile compounds. The amount of ether-extractable carbon was on the order of 10% to 14%; ethyl acetate extracted an additional 3% to 4% of the original carbon. The portion of this extractable carbon that was also chromatographable was not determined, but it was evident that identifiable products represented a small fraction of the initial fulvic material. The bulk of the organic substrate remained in aqueous solution, implying that it was not sufficiently degraded to be analyzable by these techniques, providing additional evidence that little overall reaction occurred between ClO_2 and fulvic acid.

Four major classes of compounds were represented in the degradation mixtures of both pH 3 and 7.8 reactions with ClO_2: benzenepolycarboxylic acid methyl esters, aliphatic dibasic acid dimethyl esters, carboxyphenylglyoxylic acid methyl esters, and aliphatic acid monomethyl esters. Benzene di- and tricarboxylic acid methyl esters and palmitic acid methyl ester, plus three of its branched isomers, were dominant components of the sample extracts. But these aromatic compounds were also detected in abundance in the undegraded control and therefore cannot be regarded as unique products of the ClO_2 fulvic acid reaction. Individual products or product abundances not observed in system control samples included carboxyphenylglyoxylic acids, methylfurancarboxylic acid, dibasic aliphatic acids (C_4-C_{10}), and small quantities of dichloroacetic acid, monochloromalonic acid, and monochlorosuccinic acid. The dibasic aliphatic acids were the one structural category found in greater abundance with ClO_2 than with permanganate and chlorine (2,9). The results obtained with ozone were similar to those with ClO_2, except that chlorinated derivatives were absent in product mixtures (11). The cumulative ozone demand of fulvic acid varied between 1 and 2 moles O_3 per mole carbon. For experiments in which a ratio of 5 moles O_3 per mole carbon existed, 20% of the original TOC was converted to CO_2 or other volatile products.

Of the fulvic acid degradation agents tested, monochloramine is apparently the least effective, since no reaction products were identifiable in ether extracts of reaction mixtures (12) (though fulvic acid solutions exerted a demand of 0.13 mole of monochloramine per mole of fulvic carbon after 24 hr at pH 9). Colclough et al. (2,9) observed by way of comparison that fulvic acid consumed 0.3 mole ClO_2 per mole of carbon at pH 7.8.

References

The following publications collectively contain the complete findings of this research project. The Ph.D. thesis (#1, Liao) is available from University Microfilms, P.O. Box 1346, Ann Arbor, MI 48106. Completed master's thesis (#2,3, Colclough and Norwood) are available from R. F. Christman, Department of Environmental Sciences and Engineering, University of North Carolina, Chapel Hill, NC 27514. These and articles that are in preparation (#11,12,13) are also available from R. F. Christman.

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